Controlling Interfacial Properties of Solid-State Lithium Batteries Using Atomic Layer Deposition

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Controlling Interfacial Properties of Solid-State Lithium Batteries Using Atomic Layer Deposition

Approved By:

Dr. Matthew McDowell, Advisor
George W. Woodruff School of Mechanical Engineering
Georgia Institute of Technology

Dr. Tequila Harris
George W. Woodruff School of Mechanical Engineering
Georgia Institute of Technology

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Abstract

Solid-state lithium batteries (SSLiBs) are a promising next generation energy storage device for consumer electronics, electric and hybrid vehicles, and alternative energy generation systems. Currently, interfacial impedance and instability are the primary obstacles preventing efficient operation of solid-state lithium batteries. This study uses atomic layer deposition (ALD) of thin film oxides to develop protective layers at the interface between ceramic solid electrolytes and lithium metal anodes. It is expected that these protective layers will reduce interfacial instability and impedance by improving wetting properties and preventing detrimental anode-electrolyte interactions. The project entails designing and building a custom ALD reactor, depositing thin film oxide materials, and analyzing structural and chemical changes of these materials when coating solid electrolytes. Coated membranes are electrochemically tested within SSLiBs to determine the effect of protection films on electrochemical behavior and lifetime of the batteries. This research has potential to develop stable, high energy solid-state lithium batteries as the next generation of electrochemical energy storage devices.

Introduction

Solid-state lithium batteries feature a solid electrolyte which serves as the ion conductor between the anodic and cathodic electrodes of the battery. Solid-state lithium (Li) batteries provide a safer, more efficient electrochemical energy storage means compared to their lithium-ion counterparts. Solid electrolytes are favorable compared to liquid electrolytes, commonly found in lithium-ion batteries, because of their high ionic conductivity and high energy and power density[4]. Furthermore, the use of ceramic solid-state electrolyte compared to flammable liquid electrolyte improves safety. However, successful implementation of solid-state lithium

batteries is contingent upon controlling the interfacial chemical, mechanical, and electronic properties of the solid-state electrolyte.

Research efforts towards reducing interfacial impedance and electrochemical instability have focused on characterizing interfacial electrochemical behavior between lithium metal anode and solid electrolyte ceramics. Characterization of ceramic interfaces have demonstrated the formation of reaction layers in ceramic electrolyte interfaces as well as void spaces, both key contributors to interfacial ionic impedance. The increased interfacial impedance reduces the power density of the battery as a result of the accompanying poor lithium interfacial transport[2]. Further characterizations have used the relationship between diminishing electrochemical windows of solid-state electrolytes to demonstrate the instability of solid electrolytes against lithium metal anodes[5]. These characterizations are only surface-level representations of the instability and uncertainty surrounding the interfacial properties of solid-state electrolytes. In order to mitigate the aforementioned undesirable morphology and electrochemical behavior, it is important to develop a way to control the interfacial reactions.

This study uses atomic layer deposition of thin film metals and oxides to develop protective layers at the interface between solid electrolyte NASICON-type material and lithium metal. This study involves the synthesis of ceramic membranes, as well. It is expected that this research will help lead to the identification of effective protective layer materials as well as their result on interfacial properties of solid electrolyte materials and lithium metal.

Literature Review

The focus of current research in the field of solid-state lithium batteries is the stabilization of solid electrolytes. Current research is focused on the properties and behavior of ceramic solid electrolytes, in particular. Implementation of solid-state lithium batteries is

contingent upon controlling the interfacial chemical, mechanical, and electronic properties of the solid electrolyte material. Instability, and resulting interfacial impedance, are the primary obstacles preventing efficient operation of solid-state lithium batteries. The goal of this study is to build on previous research conducted towards the understanding of electrochemical behavior in solid-state lithium batteries in order to prevent the impedance-inducing electrochemical reactions at the interface.

Research by Han et al.[1] will serve as a foundation of the current study towards understanding and resolving interfacial impedance in solid-state lithium batteries. Han et al. address interfacial impedance in garnet-based solid-state lithium batteries. Specifically, the authors aimed to reduce ionic impedance at the garnet-type LLCZN solid-state electrolyte (SSE) and lithium (Li) metal anode interface. Lower ionic impedance can improve Li-ion transport through the LLCZN solid electrolyte and Li metal interface, and thereby enable high energy density solid-state batteries. Accordingly, Han et al. propose atomic layer deposition (ALD) of aluminum oxide (Al_2O_3) as an ultrathin (5~6 nm) coating to reduce interfacial impedance. ALD of Al_2O_3 ultrathin coating on LLCZN SSE resulted in interfacial impedance reduction from 1,710 ohms·cm^2 to 34 ohms·cm^2. While other factors are hypothesized to contribute to the impedance reduction, the empirically emphasized factor is the improved interfacial contact between the garnet electrolyte and the Li metal anode. Scanning Electron Microscopy (SEM) images show that interfacial voids exist without the implementation of the Al_2O_3 coating. However, upon ALD of Al_2O_3, the interfacial conformity improves and shows no void spaces. The impact of Al_2O_3 on interfacial contact is verified by calculating the binding energy of Li metal on lithiated ALD-Al_2O_3 coating. Han et al. cite the high binding energy for the improvement of Li metal wetting on SSE, and therefore the improved interfacial contact.[1] This contributes significantly to the study

of solid-state lithium metal batteries in terms of proving the merits of ALD-Al_2O_3 at the LLCZN-Li metal interface.

While Han et. al provide reason to investigate the use of garnet-based solid-state electrolytes further, Zhu et al.[5] make the case for oxide-based electrolytes by demonstrating an effected material selection method. Zhu et al. present their findings on solid electrolyte stability in terms of their electrochemical window. Specifically, Zhu et al. point to the formation of decomposition interphases and artificial coating layers. According to Zhu et al., the decomposition interphases are stable against lithium metal, allowing them to negate the effect of the chemical potential difference between the lithium metal electrode and the solid electrolyte. As a result, the stability of the solid electrolyte is improved. The authors cite the implementation of artificial coating protective layers as a means to extend the anodic and cathodic limits to increase the interfacial stability.[5] The calculations performed by the Zhu et al. could contribute to our material selection in our synthesis of solid-state lithium battery systems. Furthermore, this research could guide our tailoring of electrolytes for high stability against Li metal.

In terms of methodology, atomic layer deposition is the hypothesized to be the best method of developing our interfacial protective layers. This is evident given the methods used by the study by Kim et al.[2] Kim et al. examined the interfacial characteristics of $Li_7La_3Zr_2O_{12}$ (LLZ) solid-state electrolyte and $LiCoO_2$ thin films. The research focused on electrochemical characterization when $LiCoO_2$ was deposited on LLZ using pulsed laser deposition. The experiment found poor electrochemical performance at the interface. Specifically, cyclic voltammetry was used to determine that there was insufficient lithium insertion and extraction at the interface of LLZ and $LiCoO_2$. Kim et al. used transmission electron microscopy to determine the formation of a reaction layer at the interface, which is cited as the cause for the poor lithium

interfacial behavior. The resistance due to the LLZ-$LiCoO_2$ reaction layer results in reduced power density due to inefficient Lithium transport across the interface. The formation of the reaction layer, occurring during the deposition process, is critical to address in order to enable efficient electrochemical performance.[3] This work is applicable directly to the current research study because it examines the interfacial characteristics of a ceramic-based solid electrolyte (LLZ) and oxide thin films ($LiCoO_2$). However, the approach of Kim et al. to this problem uses high-temperature pulsed laser deposition, a directional deposition process. [2] The current study will utilize atomic layer deposition, a conformal deposition process, to perform the same syntheses. This could have significant advantages towards better protection of the solid electrolyte materials. Since selection of interfacial protective material is a primary concern of the current study, the work of Liu et al.[3] played an important role in terms of identifying lithium tantalate as a promising candidate to further investigate.

The goal of the study by Liu et al. was to use ALD to synthesize lithium tantalate thin films that had effective Li-ion conductivity without high-temperature annealing and post-annealing processes. The post-annealing process increases the risk of cracking in the film which can be detrimental for battery operation. Liu et al. hypothesized that atomic layer deposition of lithium tantalate could achieve an acceptable level of ionic conductivity (10^{-5} – 10^{-8} S/cm), without the aforementioned risks, by configuring the thickness and the film composition accordingly. ALD of lithium tantalate resulted in a Li-ion conductivity of 2 x 10^{-8} at the as-deposited state. In addition, the lithium tantalate films showed conformal coverage on a 3-D anodic aluminum oxide substrate.[3] The lithium tantalate could be used as an interfacial protective layer in our solid-state lithium batteries, if the oxides and metals currently considered demonstrate high risk of structural failure due to post-annealing. The lithium tantalate is proven

to conduct Li-ions at the as-deposited state, so there would be no need for further treatment. This material could serve as another option in the event of structural failure of the oxide and metal thin films that we will be testing in solid-state lithium batteries.

The current study focuses on ALD of oxide materials for ceramic solid-state conductors, similar to the work of Han et al. The findings of Han et al. serve as a building block toward characterizing interfacial reactions between lithium metal anodes and ceramic solid-state electrolytes, as well as towards understanding the role of oxide thin film materials for stabilizing high-energy batteries. The current study will further this research by evaluating the electrochemical effects of other oxides such as SiO_2, as well as metal coatings such as Molybdenum and Tungsten. Furthermore, performing a similar study as Kim et al. with the new deposition process (ALD) will yield a better understanding of the aforementioned ceramic solid electrolyte and thin film interactions as it relates to the formation of reaction layers. It is expected that this study will lead to the identification of compatible solid electrolyte materials as well as coating materials.

Methods and Materials

The goal of this research project is to stabilize traditionally unstable interfaces between lithium metal and ceramic electrolytes to improve SSLiB performance. Atomic layer deposition (ALD) is a thin film growth technique that allows for nanoscale thickness control of deposited oxide materials. This project uses ALD of thin film oxides (Al_2O_3) to develop protective layers at the interface between $Li_{1.4}Al_{0.6}Ge_{1.4}(PO_4)_3$ (LAGP) solid electrolytes and lithium metal. This project entails building a custom ALD reactor, depositing thin film materials, and analyzing structural and chemical changes of these materials when coated on solid electrolytes and used in batteries. This project includes testing coated membranes within SSLiBs.

Temperature Controller

Design and assembly of the ALD instrument is the first phase of the research project. The primary ALD sub-systems are the vacuum flow system, pneumatic control system, and temperature control system. These sub-systems are developed around the reaction chamber where coating materials are deposited.

In order to monitor and regulate chamber temperature, a temperature control unit was developed. Figure 1 shows the constructed temperature controller. The temperature controller required implementation of a circuit design enabling communication between an Omega Engineering CN7800 series temperature controller and relevant components. The temperature control box features four CN7800 series controllers with accompanying circuitry. The circuit for a single controller includes a solid-state relay as an ON/OFF switch, a fuse to provide overcurrent protection, power inlet and outlet connectors, as well as a K-type thermocouple junction. The thermocouple serves as the sensor for pipe temperature with measurements displayed on the controller.

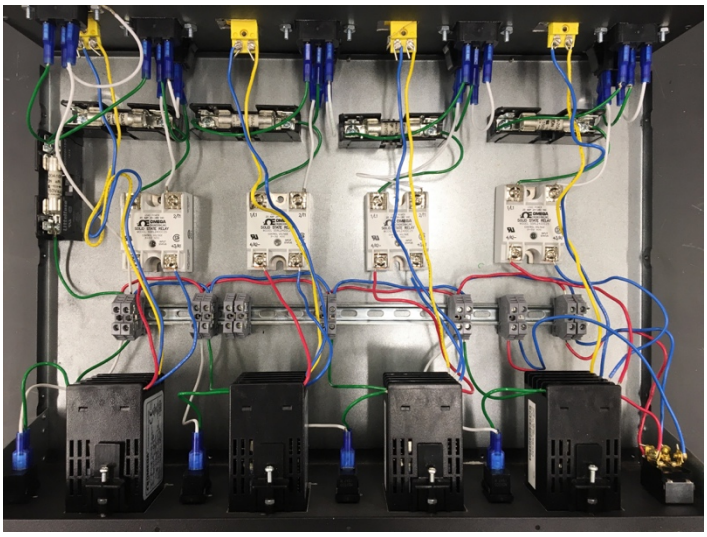

Figure 1: Temperature Control Box

The chamber and pipes are heated during flow of precursor gases using fiberglass insulated heating tape which provides fast, high temperature thermal response. This heating mechanism interfaces with the Omega control module, enabling user input to ramp chamber temperatures. Four such circuit assemblies were implemented in parallel to complete the ALD's temperature monitor and control unit.

Pneumatic Control System

Development of the reactor's pneumatic control system is the second phase of the research endeavor. Figure 2 shows the constructed pneumatic control box. The control unit enables and restricts precursor flow to the reaction chamber where the substrate is exposed to precursor chemicals for materials deposition. The hardware of the control box includes 2 OnTrak ADR2200 microcontrollers to manipulate 16 solenoid valves.

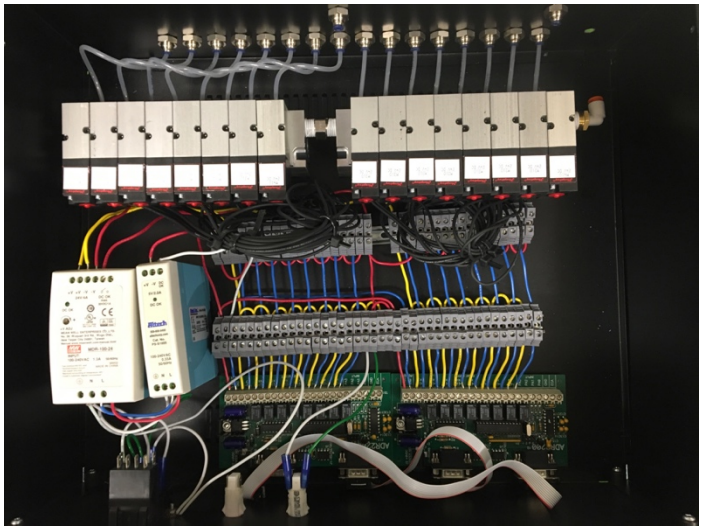

Figure 2: Pneumatic Control Box

Accordingly, the ALD is designed to release up to 16 precursors, sequentially, as necessary. Nitrogen gas is run through 2 manifolds connected to the solenoid valves, and

available to the valves as needed. Tubing connects the solenoid valves to ALD-specific valves from Swagelok. These valves were chosen for their rapid, precise release of precursors.

In addition to hardware, a LabVIEW Virtual Instrument (VI) was developed to control actuation of the solenoid valves. Figure 3 shows the user interface of the program. The VI uses RS-232 serial communication to deliver commands from LabVIEW to the microcontrollers. Depending on user inputs, a zero or one and a port ID sequence are relayed to the controllers. The port corresponding to the desired solenoid valve is activated, sending current to the valve. Upon receiving current, the valve is opened and remains open until user input stops the current flow. Next, ultra-high purity nitrogen flows to the ALD valve on the precursor containers. The result is that each ALD container has a corresponding solenoid valve, port on the OnTrak controller, and switch on the VI's user interface. The developed VI pulses each valve for 0.1 seconds at intervals of 15 seconds to release different precursors for nanoscale thickness control.

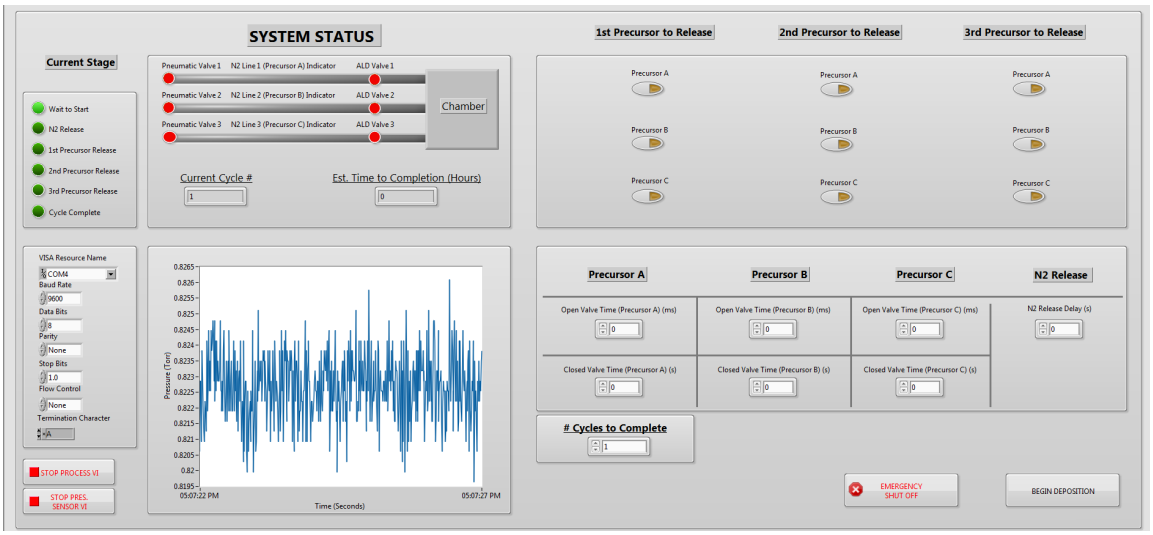

Figure 3: LabVIEW User Interface

In addition, the VI accommodates an MKS Baratron absolute capacitance manometer for real-time pressure readout and control. Implementation requires converting output voltages to units of pressure in accordance with the gauge's specifications. The goal is to produce a real-time

pressure versus time plot during the ALD process. Moreover, the VI is developed to ensure operation within safety parameters. Emergency shut-off procedures are to be introduced in accordance with read-outs from the chamber's pressure transducer.

Reaction Chamber

For the final build stage, detailed schematics for the chamber design were produced and executed as shown in Figure 4. Valves, piping, pumps, and containers for the system were then incorporated to the assembly. Furthermore, the final process entails implementing mass flow controllers and Swagelok diaphragm valves along piping for flow control. This process includes fabrication of aluminum framing to mount all ALD components. CNC machining equipment was used in the Montgomery Machining Mall at Georgia Institute of Technology for the construction process. Steel tubing was welded using tungsten inert gas welding with guidance from graduate student Collen Leng of Dr. Mark Losego's lab at Georgia Institute of Technology. Figure 5 shows the entire ALD system.

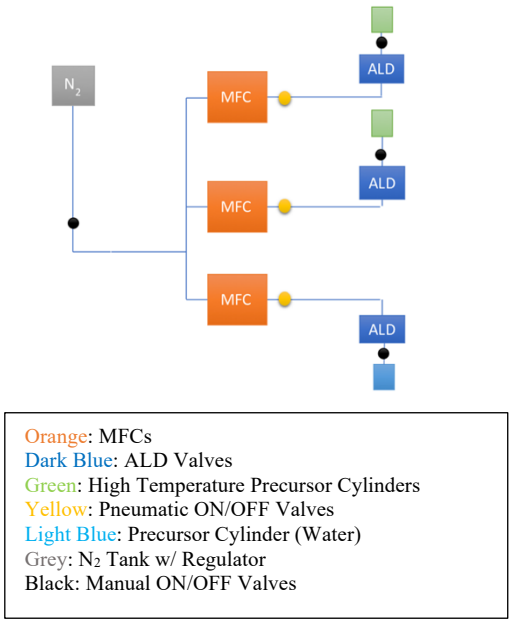

Figure 4: ALD Flow Control Schematic

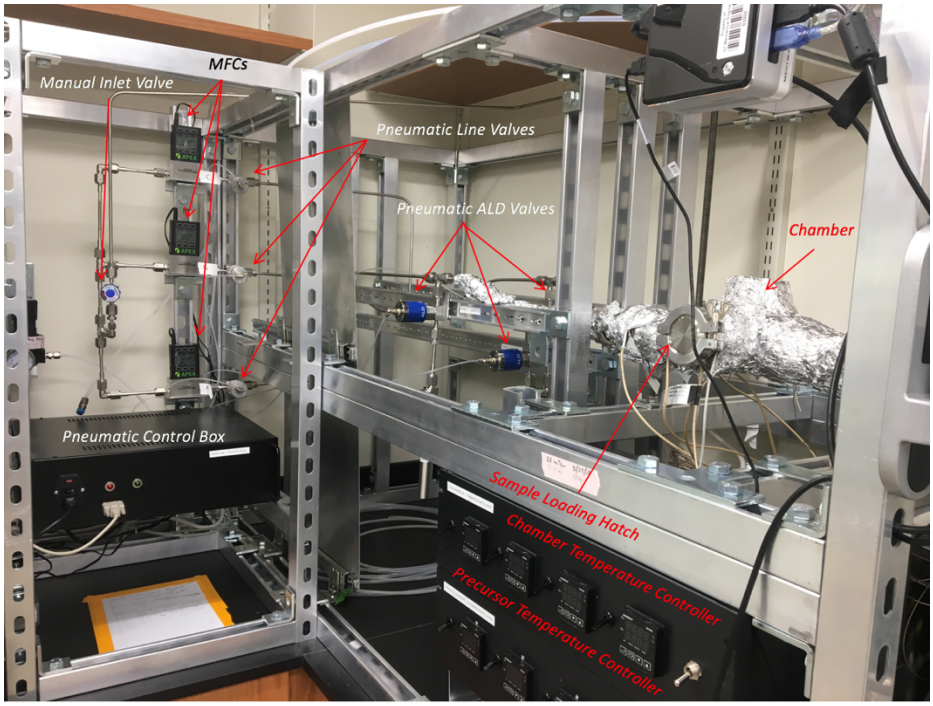

Figure 5: Completed ALD System

Oxide Deposition

The next phase of the research project is deposition of oxide thin film materials using the custom ALD reactor. The reactor is used to coat NASICON-type material $Li_{1.4}Al_{0.6}Ge_{1.4}(PO_4)_3$ (LAGP). Figure 6 shows a scanning electron microscopy (SEM) image of LAGP used in the experiment.

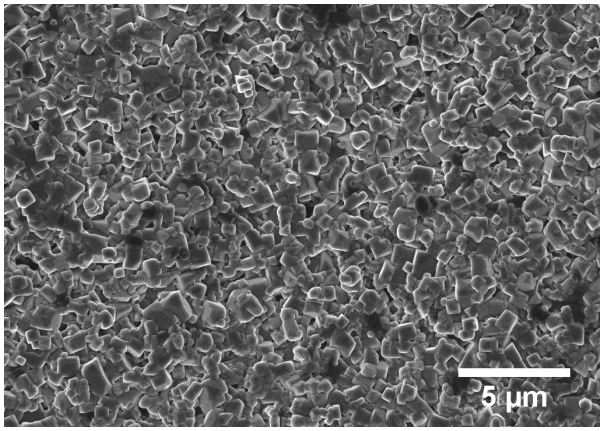

Figure 6: SEM of $Li_{1.4}Al_{0.6}Ge_{1.4}(PO_4)_3$ (LAGP)

This solid electrolyte has a high ionic conductivity of ~1-5 x 10^{-4} S/cm making it ideal for study in SSLiBs. However, LAGP is challenged by its thermodynamic instability against lithium which leads to high impedance interfaces. Modifying the Li/LAGP interface using ALD could provide stability and lead to improved performance. LAGP is coated with Al_2O_3 to improve stability and electrochemical performance. The custom ALD is used to coat LAGP with 2nm and 6nm of alumina. Figure 7 shows the deposition process using trimethylaluminum (TMA) and H_2O as precursors to form layers of alumina on the surface of LAGP.

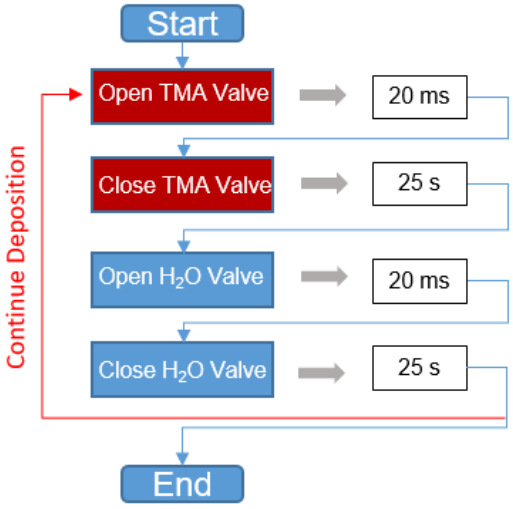

Figure 7: Valve Functionality for Alumina Deposition

To form alumina, TMA is released for 20ms into the chamber. After a 25s period, water is released to the chamber for 20ms. This valve remains closed for 25s after which time the cycle repeats. This process represents a single ALD cycle. This system deposits 1nm of alumina for every 10 ALD cycles. The substrate is exposed to precursors at 150°C and 0.06 torr. 2nm and 6nm of alumina are coated on LAGP and compared to bare LAGP within SSLiBs to determine how alumina affects electrochemical performance. Different alumina thicknesses are investigated to determine the optimal coating thickness.

Electrochemical Testing

After deposition, symmetric lithium coin cells were created using 2nm and 6nm alumina-coated LAGP. A schematic of this cell design is shown in Figure 8.

Figure 8: Lithium Symmetric Cell

These cells were cycled at 0.2 mA/cm^2 to determine the overpotential and lifetime. The effect of the alumina protection films on electrochemical behavior and lifetime are compared to that of uncoated LAGP in solid-state lithium batteries. These techniques are used under the instruction of Mr. Cortes and PI Dr. Matthew McDowell in the Materials Characterization Facility. This phase of analysis determines whether the ALD coating improves interfacial wetting.

Results

Cells having bare LAGP, 2nm of alumina on LAGP, and 6nm of alumina on LAGP were cycled. The resulting electrochemical performance and lifetime was examined. Figure 9 (a-b), Figure 10 (a-b), and Figure 11 (a-b) show voltage as a function of time for bare LAGP, 2nm of alumina on LAGP, and 6nm of alumina on LAGP respectively. These cells were tested at constant current to investigate the effects of alumina coatings on overpotential and impedance.

Bare LAGP

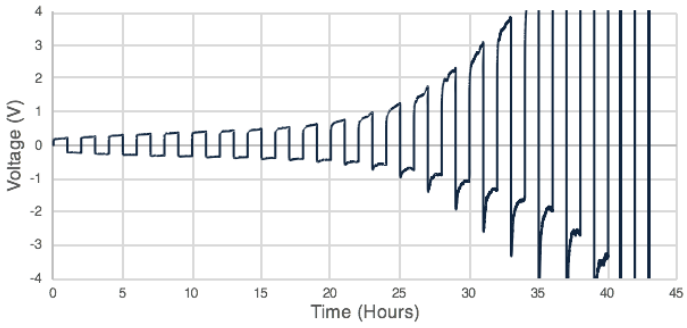

Figure 9a: Bare LAGP Cycling

Bare LAGP

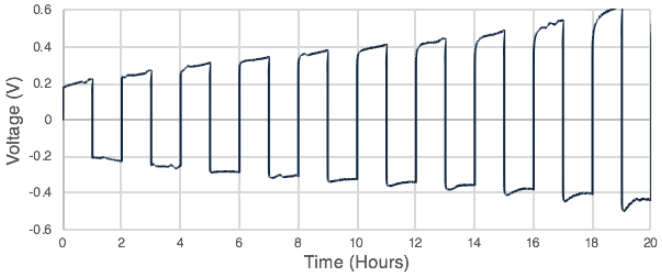

Figure 9b: Bare LAGP Cycling

Figure 9a shows that bare LAGP cell failed after 44 hours and Figure 9b shows that bare LAGP had a low overpotential of approximately 0.2V. However, this cell was not stable over time as is shown in Figure 9b. These results indicate that impedance and interfacial instability increase over time.

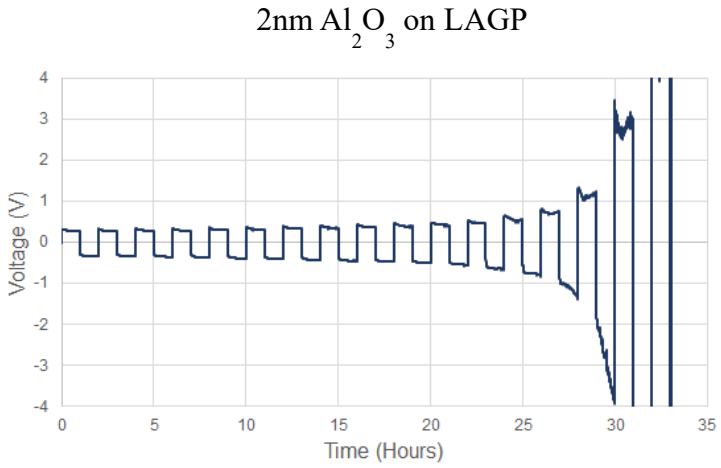

Figure 10a: 2nm Al_2O_3 on LAGP Cycling

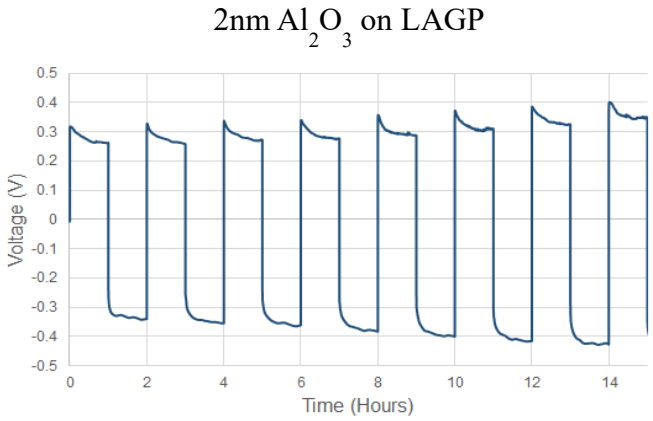

Figure 10b: 2nm Al_2O_3 on LAGP Cycling

Figure 10a shows that 2nm of alumina on LAGP resulted in a cell lifetime of approximately 34 hours. Figure 10b shows that this cell has an overpotential of 0.3V. Additionally, Figure 10b shows better stability over time as compared to bare LAGP as this voltage remains relatively consistent over the first 10 hours. This suggests that adding an interfacial layer of alumina results in improved cell stability during cycling, while maintaining a low overpotential. This is a concern because adding an insulator such as alumina can increase overpotential and thus increase impedance for ion transport through the interface.

6nm Al_2O_3 on LAGP

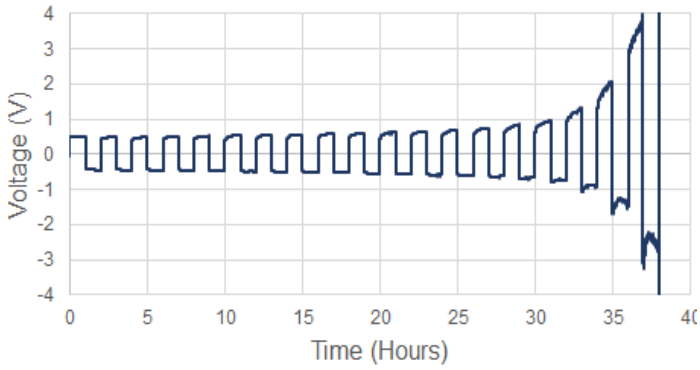

Figure 11a: 6nm Al_2O_3 on LAGP Cycling

6nm Al_2O_3 on LAGP

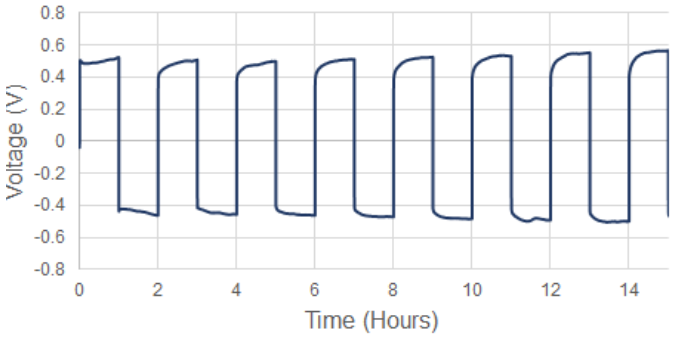

Figure 11b: 6nm Al_2O_3 on LAGP Cycling

To further investigate the effect of adding alumina, 6nm of alumina was deposited on LAGP and the SSLiB was tested. Figure 11a shows that 6nm of alumina resulted in a lifetime of approximately 48 hours. Figure 11b shows that this cell was most stable over the first 10 hours. Nevertheless, adding 6nm of alumina increased the overpotential to 0.5V as shown in Figure 11b. This is expected since the impedance should increase with adding more alumina and thus increase the overpotential.

Discussion

The atomic layer deposition instrument was completed to specifications of 1 angstrom deposition thickness. The instrument, tailored for both binary and ternary ALD processing, with precursor release patterns of $(A\text{-}B)_x$ or $(A\text{-}B\text{-}C)_x$ of oxides allows for complex, custom thin film layers and laminates to be added to the desired substrate. Comparing Al_2O_3 of 2nm and 6nm with bare LAGP cells, it is evident that alumina protection layers do not have a significant or meaningful impact on the lifetime of the cells. Nevertheless, it is clear that the oxide protection layer does impact the shape of the cycling curves and their growth over time. Specifically, adding thicker layers of alumina, such as 6nm, increases the stability over time – that is, the electrochemical curve remains relatively consistent for approximately 25-30 hours. By comparison, 2nm of alumina maintain stability for nearly 20-25 hours. While the 2nm is less stable over time, the overpotential is less than that of the 6nm cell. This tradeoff suggests that increasing thickness of alumina causes interfacial impedance – that is, ion transport becomes more difficult through this interface. Nevertheless, alumina does contribute to stability over time when comparing protected LAGP to bare LAGP.

Conclusion

The results of this study show that the custom ALD tool described can be used to improve solid-state lithium batteries by coating NASICON-type material LAGP with alumina. While this study found that alumina does not impact the lifetime of lithium symmetric cells, overpotential and thus impedance can be improved by adding this oxide protection layer. These findings are consistent with those presented in current literature. This project also finds that there is a tradeoff between interfacial ion transport and the stability of the cell over time. Improving cell stability with more alumina insulator causes increased impedance. These results suggest alumina alone is

not the optimal solution to solving interfacial impedance and performance of solid-state lithium batteries. A potential avenue for further research is combining this insulating layer with conductive layers. It is hypothesized that striking a balance between 2-6nm alumina with a conductive protection layer could improve solid-state battery performance by lowering overpotential, improving ion transport, and increasing stability and lifetime of these batteries.

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